The Vapour Pressure in Equilibrium with Substances Holding Varying Amounts of Moisture.

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PART I.

The knowledge of the quantity of water held under varying circumstances by substances of an absorbent character, such as cotton or woollen material, in an atmosphere of any given humidity, is not only of importance in hygrometry, but is also of general interest in connection with the processes used in drying such materials. No investigations, however, of this subject seem up to the present to have been ever published.

Some years ago, while making a series of comparative determinations of the weight of moisture absorbed out of the atmosphere by different kinds of fabrics, two interesting points were noticed. The first was that the weight of water absorbed or held by a given material under different conditions of moisture and temperature of the atmosphere, appeared to depend only on the hygrometric state (*i.e.*, the ratio of actual vapour pressure to the maximum possible), though of course the actual amount of moisture present in the atmosphere for the same ratio is very different at different temperatures. The second point noticed was that as the atmosphere varied from saturation, the temperature remaining the same, the amount of water held followed some law giving much greater reduction in weight for a given change in vapour pressure when near saturation than is subsequently obtained. As described below, this law ultimately proved to be a simple parabolic one, at least until approaching desiccation.

Early Experiments.—The first experiments were made in the following way, and though they were subsequently found not to be capable of sufficient refinement, as far as they went they served to suggest the above relations. The material used was first desiccated in the presence of air over phosphorus pentoxide, and its weight ascertained. The latter was done in the open air, so that the weight continually augmented through condensation of moisture. To get the initial weight a curve was plotted of weight against time, and extrapolated to the first moment of exposure to the atmosphere. The material was simply left exposed to ordinary atmospheric conditions, and its weight observed from time to time, the hygrometric state of the atmosphere being found simultaneously by a wet and dry bulb instrument. These determinations were carried on for some months, a reading being made each day. From these a few of the more striking cases are given in Table I, illustrating the first relation. These have been selected in pairs, so that the weight (W) held in the material is approximately the same, while the amount of moisture in the air is very different, as shown by the vapour pressure (p), but in each case it will be seen that the hygrometric ratio is also approximately the same, *i.e.*, the ratio of (p) the vapour pressure in the atmosphere to P the saturation pressure for the temperature (t) at the time.

This relation may then be shortly written as $W = f(p/P)$.

Table I.

W.	p.	t.	P.	p/P.
0·58	0·92	13°·4	1·14	80
0·60	0·61	7·6	0·77	80
0·53	0·82	12·6	1·08	76
0·56	0·55	6·6	0·72	77
0·52	0·46	4·8	0·64	73
0·53	0·78	12·2	1·05	75
0·42	0·85	14·8	1·24	69
0·45	0·55	7·7	0·79	70
0·36	0·59	9·7	0·89	67
0·37	0·98	17·4	1·47	67
0·30	0·97	18·2	1·55	63
0·30	0·60	10·8	0·96	63

Subsequently accurately devised experiments, carried out by Miss B. Pool, and given in Part II of this paper, have proved this relation, which indeed can be shown from thermo-dynamic considerations to necessarily hold, at least within usual atmospheric ranges.

Thermo-Dynamic Considerations.—To show this, some of the material may be imagined placed under a piston in a cylinder containing water vapour, and a cycle of the usual type passed through. Let the material holding the requisite weight of water be in equilibrium with the vapour at a pressure less than the maximum of saturation pressure. First an isothermal expansion takes place from volume v_1 to v_2, evaporation of fresh vapour from that in the material will take place, but if the amount required is small in comparison to that in the material, the pressure may be taken as remaining constant. Let w be the weight thus evaporated. The heat required for the evaporation is λw, where λ is the latent heat of vaporisation under the conditions of the operation. Secondly, let an adiabatic expansion cool the contents of the cylinder through $\delta\tau$ degrees, the pressure falling in consequence δp. Thirdly, the volume is isothermally compressed the proper amount to admit of the cycle being completed in the fourth stage by an adiabatic compression.

We thus have, by Carnot's principle,

$$\frac{(v_2-v_1)\,\delta p}{\lambda w} = \frac{\delta \tau}{\tau}.$$

But $$w = (v_2-v_1)\,\rho p/\text{P},$$

where ρ is the density of the saturated vapour at temperature τ. Hence

$$\frac{\delta p}{\delta \tau} = \frac{\lambda\rho}{\tau}\cdot\frac{p}{\text{P}}; \qquad \text{but} \qquad \frac{\lambda\rho}{\tau} = \frac{\delta \text{P}}{\delta \tau},$$

assuming that λ is the same in the two cases, where P is the saturation pressure at temperature T; so that we may write

$$\frac{dp}{d\tau} = \frac{p}{\text{P}}\,\frac{d\text{P}}{d\tau}.$$

That is to say, the slope of the curve* giving for different temperatures the pressure in equilibrium with the material wetted with a constant weight of water, is to that of the ordinary vapour pressure curve in the ratio of the ordinates which represent the pressures. This necessitates the pressure being proportional to the saturation pressure, or $p = \text{K.P}$. That is to say, however the temperature changes, if the hygrometric state (p/P) is kept constant, the weight of water held by the material remains constant.

It is convenient to have a name for the curves on the pressure-temperature diagram, which are drawn so that the pressure is always a constant fraction of the saturation pressure. These curves throughout this paper will be called *isohygrometric* curves. It is also convenient to have a term for the curve drawn giving at different temperatures the pressure of vapour from a substance wetted with or holding a constant weight of water. These curves are called in the paper *isoneric* curves (from *νηρος* moisture, already in use in aneroid), or shortly *isoneres.* The considerations given above would show that approximately the isoneres coincide with the isohygrometrics. It will be shown later that in the case of solutions, when one body is non-volatile, the same relation may be considered approximately to hold.

Second Relation.—Some indication of the second relation, namely, the function W is of p/P, was got from the original set of experiments, although the range under atmospheric conditions is necessarily very limited. As typical of the general results, the following Table II is given, which is compiled from observations made with a specimen of flannel. Owing to the uncertainty of the observations, and the variation among themselves (most probably due to the unsatisfactory method adopted for ascertaining the vapour pressure, namely, the wet and dry bulb thermometers), they have been massed in groups round a mean value of the corresponding hygrometric states.

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* See fig. 9.

In the first column is given the mean hygrometric state of each group; in the second column the corresponding mean weight of the flannel; while in the third column are the calculated values of the square of the difference in weight between the latter and that of the flannel at saturation (W_1) divided by the difference between 100 and the mean hygrometric state. These are seen to be approximately constant, except in the first two or three cases. This discrepancy may be due to there having being insufficient time for equilibrium to set in, because from subsequent experiments it appears that the discrepancy from the parabolic law tends rather to the other side at low pressures:—

Table II.

H. S.	W.	$\frac{(W_1-W)^2}{100-\text{H. S.}}$.	H. S.	W.	$\frac{(W_1-W)^2}{100-\text{H. S.}}$.
47·4	17·334	0·038	74·6	17·588	0·052
59·1	·392	0·044	76·0	·702	0·046
62·5	·408	0·047	76·6	·616	0·054
63·5	·424	0·048	77·8	·652	0·053
65·2	·443	0·049	80·0	·692	0·056
67·3	·470	0·050	81·3	·760	0·054
68·5	·512	0·048	100·0	18·750	Saturated
70·4	·545	0·049	0	17·090	Desiccated
73·4	·572	0·052			

First Apparatus Used.—The method described being dependent upon the changes in the atmosphere, is obviously inconvenient and uncertain, as among other sources of error, during rapid changes in atmospheric conditions there is not time for equilibrium to set in. In order to make experiments under conditions of complete control in respect to the amount of moisture present in the surrounding atmosphere it is necessary to work in an enclosed space. This renders it impossible to use the wet and dry bulb hygrometer for determining the vapour pressure. A form of dew point instrument was therefore used, in which the deposition of moisture was ascertained by electrical means. This form was adopted because the conditions of the apparatus rendered it impossible to observe by eye the moment of deposition in the usual manner.

The arrangement consists essentially of two independent ribbons or wires of platinum wound at a small distance apart over the glass surface on which condensation of the moisture is to take place, and these are fused on the glass. The outside of a test tube is used for this purpose and a circulation of iced water, maintained in the test tube by tubes leading from a reservoir, served, when required, to produce the necessary lowering in temperature for making an observation. A sensitive galvanometer and cell are connected up with the ribbons as electrodes or poles.

While dry no current is indicated, but as soon as deposition of moisture takes place one is observed. It is of interest to note that previous to the regular observational "deposition," premonitory symptoms are always to be seen in the form of slight indications given by the galvanometer.

The vessel in which the material under examination was placed was of tin plate, double walled, and had a circulation of water constantly maintained through the space between the walls from a tank or boiler kept at a constant temperature. The temperature of the tank was kept constant by means of a thermostat placed in the vessel itself, and which controlled the flame heating the boiler.

A small hole in the top of the vessel allowed of suspending the material under examination by a fine wire from a balance, placed for the purpose overhead. In this way the weight of water at any given degree of moisture of the atmosphere in the vessel could be determined. A small aperture was also provided for introducing water when it was desired to alter the hygrometric state in the vessel.

Second Apparatus Used.—From various causes no very satisfactory work was obtained with this arrangement, and it was subsequently abandoned for an apparatus in which, instead of weighing the amount of water in the material for given hygrometric conditions, the weight is gradually increased by definite increments by supplying known weights of water to the material and the corresponding equilibrium pressure observed. In these experiments, in order to avoid other sources of error, no attempt was made to keep the temperature constant by a thermostatic arrangement, as in the previous apparatus, but instead the observations were reduced to a common temperature by means of the first relation.

The method consists essentially in enclosing the dried material in a vessel freed from air, and into which can be fed as required equal weights of water until saturation is produced. The pressure of the vapour when equilibrium has been established is read after each feed, and the experimental relation is obtained, after reduction to a common temperature, giving the pressure in equilibrium with the material when holding varying amounts of water, that is to say, the isothermal on the weight-pressure diagram.

The apparatus may be described shortly as a barometer with an enlarged top to hold the wetted material under examination, and a tube with a stopcock serving to introduce from time to time a supply of water of measured amount to the material.

A general view of the apparatus is given in fig. 1. The bulb contains the material. From it a tube passes down into a bath of mercury to form the pressure gauge. A drying tube, A, containing phosphorus pentoxide, leads to the air pump. The measured feed of water is introduced by the tube B. The amount supplied at each feed is that held in the fine tube lying between the two taps.

It is necessary that the water so introduced should be free from dissolved air. This is clearly effected, since it is supplied from a reservoir formed by the space over the mercury at the top of a "barometer" tube, and into which air free water can be originally introduced. The method of giving a feed is to shut the upper tap, open the lower tap, and raise the mercury dish which is connected by a flexible tube. In this way the fine tube is filled with the water. The lower tap is then closed and the upper opened. The tube is connected to the bulb by a mercury sealed joint, the opening left when the tube is removed serving the purpose of introducing the specimen of material under examination.

At the earlier stages of an experiment the water in the finer tube on opening the upper tap passes over, and is absorbed almost with violence, but as the material gets nearly saturated the process is slow, and it becomes necessary to drive over the water from the fine tube by carefully warming the lower end of the fine tube with a small flame.

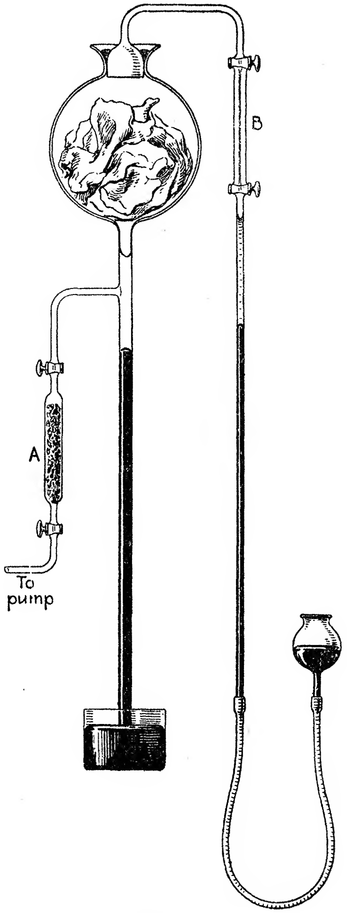

FIG. 1.

In setting up the apparatus freshly boiled water is drawn over on top of the mercury into the feed tube, and the tap closed. On lowering the mercury dish so as to leave a space over the water, more air is invariably found to be given off. This air is then ejected through the taps. It is necessary to repeat this process a number of times before all the air is removed. In preparing for an experiment it was found to require several days to dry the material, and to get it quite free from air, which apparently continues for some time to be given off by it.

There is no further object in getting rid of all air than to avoid a troublesome temperature correction.

Experimental Results.—The results of the first series of experiments, which lasted over several weeks, are exhibited in Table III. These were made with a piece of flannel 275 square centimetres, and weighing 7·30 grammes. In the second column is given the weight of water (*i.e.*, the sum of the feeds up to the time in question) introduced into the flannel, in terms of that held by the capillary tube taken as unit. A certain amount of the water supplied was required to fill the bulb with vapour up to the pressure at the time, but this was negligibly small compared to the amount in each feed. In the third column is the pressure obtained after each feed. At least 12 hours were always allowed to elapse before a reading was made, so as to insure equilibrium being established. In the fourth column is the temperature, and in the fifth is given the pressure at 20° C., calculated by assuming the truth of the first relation; that is to say, by assuming that the ratio of the pressures for two different temperatures is in the ratio of the saturation pressures, provided the same weight of water is present in the flannel.

Table III.

Date.	Weight.	Vapour pressure.	Temp.	Pressure reduced to 20° C.
July 20......	0	0·109	21°·8	0·098
„ 21......	1	0·164	21·4	0·150
„ 22......	2	0·272	21·1	0·254
„ 23......	3	0·406	21·8	0·363
„ 25......	4	0·540	21·6	0·489
„ 26......	5	0·670	20·6	0·646
„ 27......	6	0·800	20·0	0·800
„ 28......	7	0·897	19·6	0·919
„ 29......	7·8	1·044	20·3	1·025
Aug. 4......	8·8	1·343	23·5	1·085
„ 5......	9·8	1·383	22·1	1·216
„ 6......	10·8	1·328	20·5	1·287
„ 10......	11·8	1·485	21·4	1·363
„ 15......	11·9	1·287	19·0	1·379
„ 17......	12·9	1·279	18·0	1·449
„ 23......	13·9	1·247	16·9	1·513
„ 30......	14·9	1·607	20·5	1·558
Sept 16......	15·9	1·315	16·7	1·617
„ 17......	16·8	1·309	16·2	1·660
„ 19......	17·6	1·266	15·6	1·669
„ 20......	18·6	1·273	15·2	1·721
„ 21......	19·6	1·223	14·5	1·730
„ 22......	20·6	1·240	14·8	1·721
„ 23......	21·6	1·227	14·1	1·736

The results were found to agree satisfactorily with the parabolic law as mentioned above. This will be seen on examining fig. 2, where the parabola $(W-w)^2 = 234(P-p)$ has been drawn, and also the experimental points from Table III. W and P are the weight and pressure at saturation. The agreement is good until the pressure falls to about 20 per cent. of the maximum value. At this point there is a distinct indication of some further action or law coming into operation. Unfortunately complete dryness had not been reached before beginning the experiments, so a second series was undertaken to further examine this peculiarity of the curve at lower pressures. The result of these experiments was to confirm the accuracy of the first series. The action producing this deviation from the parabolic law may perhaps be fittingly referred to as the supervening of a chemical attraction, so that at first on adding water to the desiccated material little or no vapour pressure is observed.*

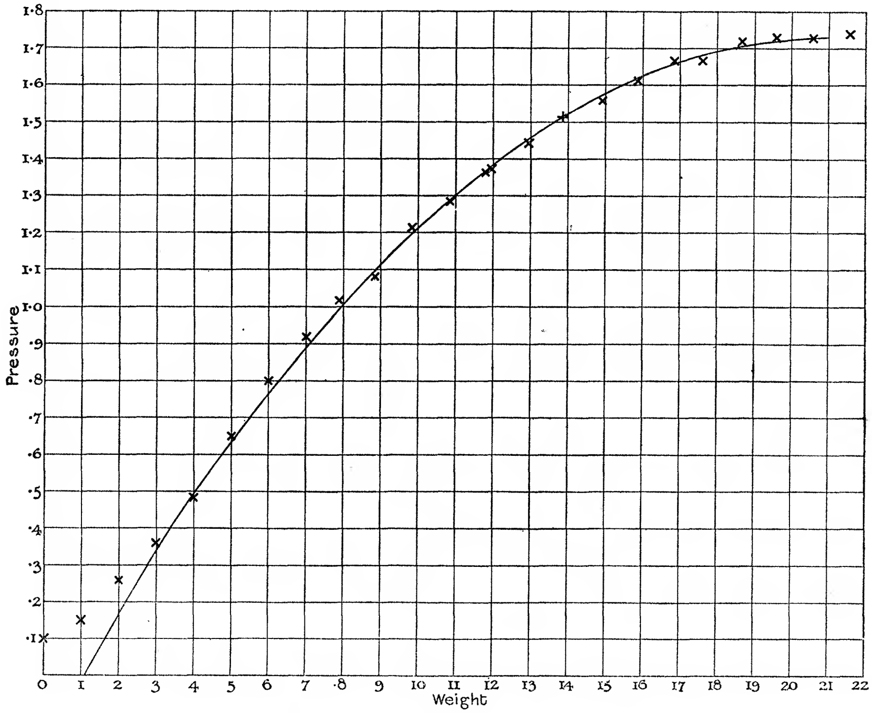

FIG. 2.—Isothermal at 20° C. for Water and Flannel.

Second Series.—Before the second series the drying was made complete. The observations are given in Table IV. The first three columns are the same as before. In the fifth column are given the pressures at 150°, calcu-

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* [*Note added February* 17, 1906.—A similar curve has now been obtained with cotton wool.]

Table IV.

Date.	Weight.	Pressure.	Temp.	Pressure reduced to 15° C.	
Feb. 4......	0	0	12°·5	0	
„ 6......	1	0·034	14·6	0·034	0·036
„ 6......	1	0·039	12·7	0·039	
„ 6......	1	0·036	14·0	0·036	
„ 7......	2	0·074	12·7	0·075	0·076
„ 7......	2	0·071	14·7	0·072	
„ 7......	2	0·077	14·2	0·081	
„ 8......	3	0·118	12·7	0·137	0·139
„ 8.. ...	3	0·140	14·7	0·143	
„ 8......	3	0·139	15·0	0·139	
„ 10......	4	0·203	15·8	0·193	0·195
„ 10......	4	0·206	15·7	0·197	
„ 10......	4	0·200	15·4	0·195	
„ 11......	5	0·200	10·7	0·264	0·258
„ 11.....	5	0·201	11·2	0·257	
„ 11......	5	0·194	10·9	0·253	
„ 13......	6	0·278	11·0	0·360	0·354
„ 13......	6	0·303	13·2	0·340	
„ 13......	6	0·313	12·8	0·361	
„ 14......	7	0·383	13·3	0·428	0·426
„ 14......	7	0·416	15·0	0·416	
„ 14......	7	0·407	14·0	0·434	
„ 15......	8	0·491	15·5	0·476	0·489
„ 15......	8	0·514	15·7	0·492	
„ 15......	8	0·467	14·0	0·498	
„ 16......	9	0·521	13·8	0·563	0·560
„ 16......	9	0·590	15·8	0·561	
„ 16......	9	0·575	15·5	0·557	
„ 17......	10	0·678	15·4	0·661	0·653
„ 17......	10	0·717	16·7	0·644	
„ 17......	10	0·670	15·4	0·653	
„ 18......	11	0·586	11·0	0·760	0·732
„ 18......	11	0·565	11·1	0·728	
„ 18......	11	0·544	11·4	0·688	
„ 20......	12	0·592	9·6	0·843	0·818
„ 20......	12	0·663	12·5	0·779	
„ 20......	12	0·704	12·4	0·833	
„ 21......	13	0·765	13·4	0·848	0·863
„ 21......	13	0·704	11·7	0·873	
„ 21......	13	0·710	11·9	0·868	
„ 22......	14	0·644	9·9	0·899	0·910
„ 22......	14	0·873	14·1	0·925	
„ 22......	14	0·775	12·6	0·905	

Date.	Weight.	Pressure.	Temp.	Pressure reduced to 15° C.	
Feb. 23......	15	0·669	9°·7	0·946	0·941
„ 23......	15	0·704	10·5	0·944	
„ 23......	15	0·685	10·3	0·931	
„ 24......	16	0·810	12·0	0·984	0·975
„ 24......	16	0·778	11·4	0·984	
„ 24......	16	0·756	11·4	0·956	
„ 27......	17	0·736	9·4	1·062	1·025
„ 27......	17	0·841	12·4	0·996	
„ 27......	17	0·847	12·2	1·016	
„ 28......	18	0·744	9·6	1·060	1·066
„ 28......	18	0·806	10·5	1·081	
„ 28......	18	0·892	12·4	1·056	
Mar. 1......	19	0·804	9·9	1·112	1·113
„ 1......	19	0·887	11·6	1·107	
„ 1......	19	0·960	12·6	1·121	
„ 2......	20	1·002	12·6	1·170	1·168
„ 2......	20	1·020	12·7	1·184	
„ 2......	20	0·998	12·8	1·150	
„ 3......	21	1·029	12·5	1·209	1·193
„ 3......	21	1·124	14·3	1·176	
„ 3......	21	1·031	12·7	1·196	
„ 4......	21·9	0·792	8·4	1·212	1·211
„ 4......	21·9	0·814	8·4	1·248	
„ 4......	21·9	0·769	8·4	1·176	
„ 6......	22·9	0·918	10·4	1·231	1·224
„ 6......	22·9	1·153	13·8	1·238	
„ 6......	22·9	1·128	13·9	1·204	
„ 7......	23·9	0·993	12·1	1·190	1·231
„ 7......	23·9	1·205	14·4	1·246	
„ 7......	23·9	1·143	13·3	1·268	
„ 8......	24·7	0·952	10·7	1·259	1·243
„ 8......	24·7	0·992	11·5	1·240	
„ 8......	24·7	1·196	14·2	1·230	
„ 9......	25·7	1·220	14·5	1·253	1·257
„ 9......	25·7	1·200	14·1	1·262	
„ 9......	25·7	1·146	13·5	1·255	
„ 10......	26·7	1·034	12·7	1·249	1·262
„ 10......	26·7	1·153	14·1	1·270	
„ 10......	26·7	1·166	14·3	1·268	
„ 11......	27·7	1·016	12·2	1·267	1·267

lated as previously by utilising the first relation. Three observations were made in each case, but in plotting the points in fig. 3 only the mean of each three is used. This series of observations does not lie on a continuous curve so satisfactorily as the first does. The first series was made during the months of July and August, when the temperature of the room in which the observations were made did not change rapidly, while the second series was obtained during February and March, when through artificial heating there was a greater daily range in temperature. A small error in temperature corresponds to a considerable variation in vapour pressure, and such an error is more likely to occur with rapidly falling or rising temperatures.

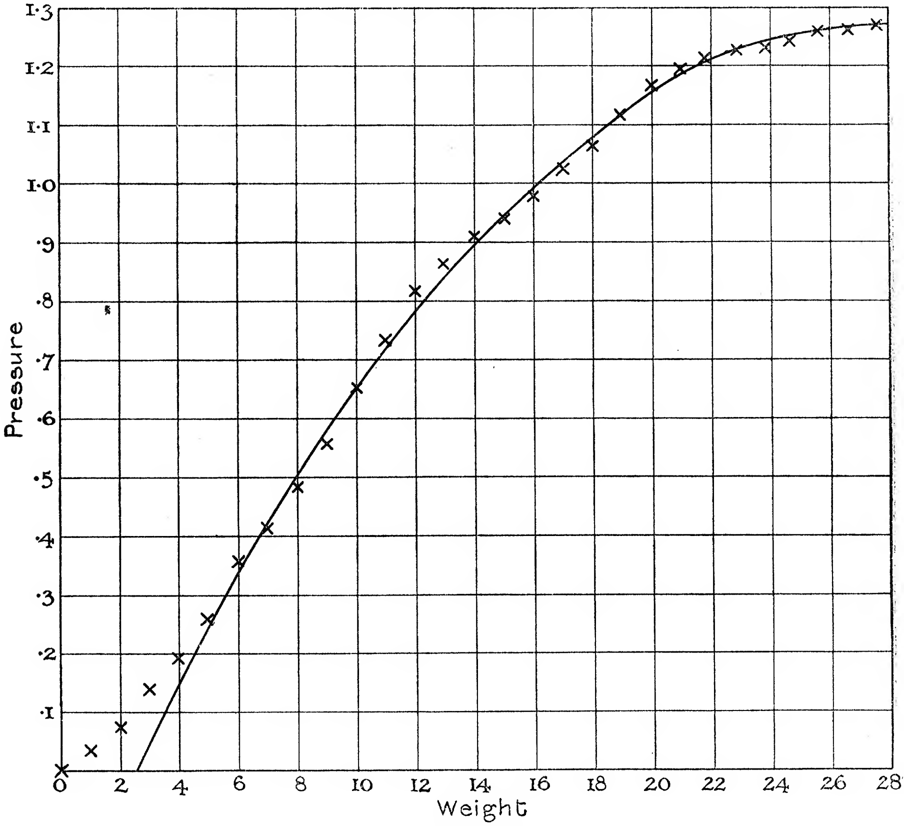

FIG. 3.—Isothermal at 15° C. for Water and Flannel.

A parabola $(W - w)^2 = 500\,(P - p)$ was found, allowing for the irregularities mentioned, to fit the points until the pressure fell to about one-fifth the maximum. This curve then, until reaching that point, may be taken as being the isothermal at 15° on the pressure-weight diagram for flannel.

On Capillary Action in the Absorbing Material.—The question is of interest as to how or in what way the water is held by the flannel or other material. No doubt some of it is held in the fine pores and cavities of the individual fibres acting as capillary tubes after the manner suggested by Lord Kelvin many years ago, as well as in those spaces lying between and formed by two crossing fibres. The following considerations show, however, that these, all put together, can only account for a small portion of the moisture except in the case of practical saturation, and that at lower pressures the moisture must be held by simple condensation on the surfaces of the material.

We can consider the cavities in the material, especially those between interlacing fibres, as equivalent on the average to a certain conical, or rather cuspoidal cavity, which gradually fills up with water as the pressure of the vapour increases. Though we may not know the shape of this cavity, we can, following Lord Kelvin's theory, calculate the diameter of the point to which water reaches in it for each given pressure. Thus

$$\mathrm{R} = 2\mathrm{T} \Big/ \left\{ \mathrm{P}_0 \frac{\rho}{\sigma_0} \log \frac{\mathrm{P}_0}{p} - (\mathrm{P}_0 - p) \right\},$$

where T is the surface tension at any selected temperature, t^0 C., ρ the density of water, σ_0 the maximum density of the vapour, and P_0 the maximum pressure at the temperature t^0.

If we knew the shape of the equivalent cuspoidal cavity we could arrive at the law connecting the weight held with the pressure. Assuming for example that the cavity is conical, we have for the law connecting W and p,

$$\mathrm{W} = \tfrac{2}{3}\mathrm{T}\pi\rho \cot\theta \Big/ \left\{ \mathrm{P}_0 \frac{\rho}{\sigma_0} \log \frac{\mathrm{P}_0}{p} - (\mathrm{P}_0 - p) \right\},$$

when 2θ is the angle of the cone.

This when plotted gives us a curve which in its general trend agrees with the experimental curve, for it is tangential to the axis of W at the origin, and is asymptotic to the saturation line. Unfortunately, however, for the capillary theory, if we calculate the radius at any pressure at all removed from saturation, we get a value which is of molecular dimensions, and at which all ideas of surface tension become unsuitable. Thus for a pressure of 90 per cent. of the saturation pressure the radius at ordinary temperatures comes out to be about $1{\cdot}2 \times 10^{-10}$ cm.

Vapour Pressure from Solutions.—It is of interest to examine the pressure of the vapour of water from solutions in liquids which themselves have practically no vapour pressure, to see if similar relations hold to those we have seen to hold for wetted solids.

Taking Regnault's results for solutions of water in sulphuric acid, it will be found that similar relations do approximately hold.

In Curve 4 is plotted the isothermal at 15° C. for water and sulphuric acid, that is to say, the vapour pressure at 15° from solutions of various strengths. The similarity of the general trend of this curve to that obtained with flannel will be noticed.

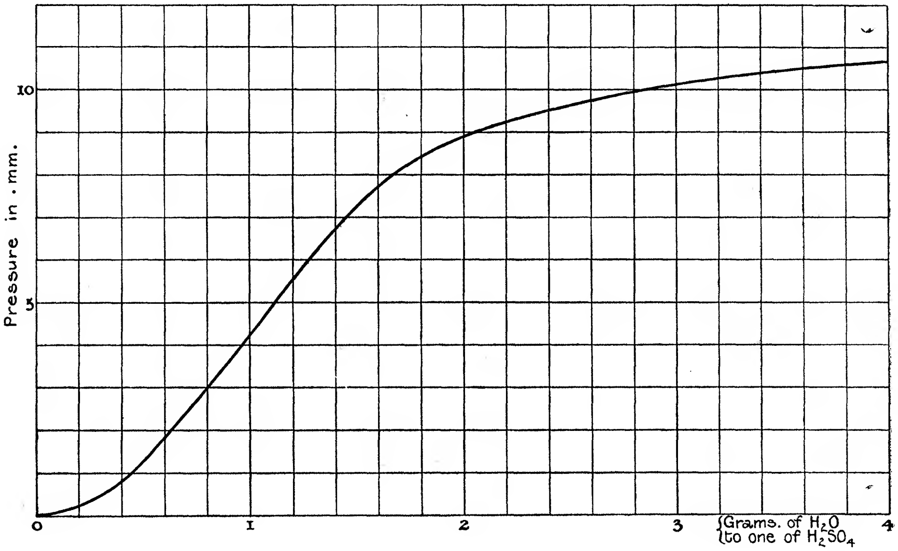

Fig. 4.—Isothermal at 15° C. for Water in Sulphuric Acid.

In the case of the solid the curve meets the saturation line at a finite distance, whereas with the liquid the approach is asymptotic. This variation in character is to be attributed no doubt to the constraint introduced by one substance being solid, so that with further accretion of water a distance is reached at which the particles of added water are outside the range of molecular attraction of the solid. On the other hand, owing to the freedom of diffusion, this constraint is not present with liquids.

The isoneres for water vapour from solutions of sulphuric acid and water are shown in fig. 5 as dotted lines. The isohygrometric curves which start from the same points at the temperature of 5° C. are also shown. These are the curves drawn with full lines.

Inspection shows that, as in the case of flannel, the two series of curves may be safely assumed to coincide, at least within the range of temperature through which Regnault worked.

Path of the Isoneres above the Critical Temperature.—At present there is no case in which we have data to enable us to draw the isoneres at relatively high temperatures. The isohygrometrics can be drawn up to the critical temperature, beyond which point they cease to have meaning. It is obvious that in general the isoneres must extend beyond this temperature. That is

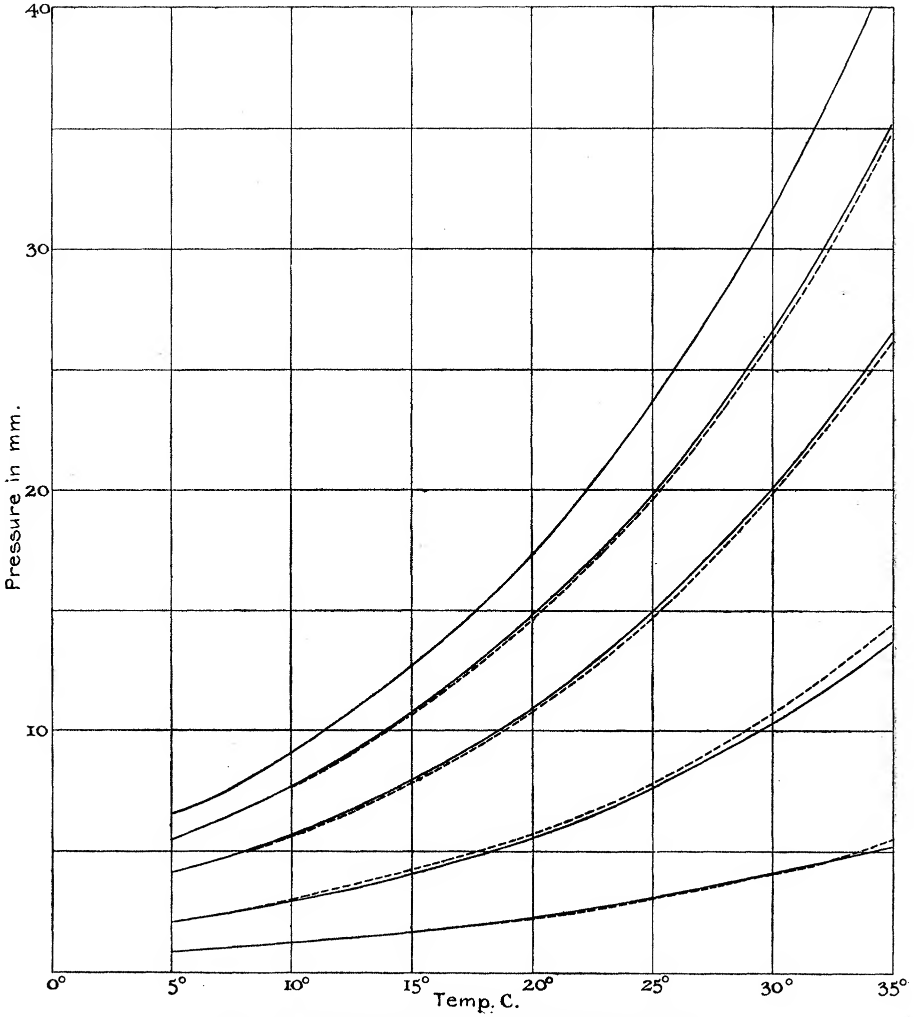

Fig. 5.—Isomers for Water and Sulphuric Acid.

to say, a curve could always be drawn giving the pressure at temperatures above the critical necessary to condense or keep from evaporating a definite weight of water on the given material. We have little information as to the condensation of water on surfaces at temperatures above the critical, but we know that similar condensation occurs with other substances, for instance, air and other gases on glass, charcoal, etc., at ordinary temperatures.

We get with some probability an idea as to how the isoneres may run at temperatures above the critical from Henry's law of the absorption of gases by liquids, namely, that the volume absorbed is constant. Thus with rising temperatures the pressure is proportional to the absolute temperature. If this is true in the case of gases and vapours condensing on solids, the isoneres at temperatures above the critical would run in straight lines passing through the origin of co-ordinates.

The exact form the isoneres take is impossible to say without further data than are at present to hand, but we may with fair probability, as indicated above, sketch out their general character. This has been done in fig. 6 for water condensing on a solid. The top line is the vapour pressure up to the critical temperature. The curved portions of the three beneath are isohygrometrics at $\frac{3}{4}$, $\frac{1}{2}$ and $\frac{1}{4}$ the saturation pressure. Assuming the coincidence of the isoneres with these, and in addition the extension of Henry's law, we have the complete isoneres as shown.

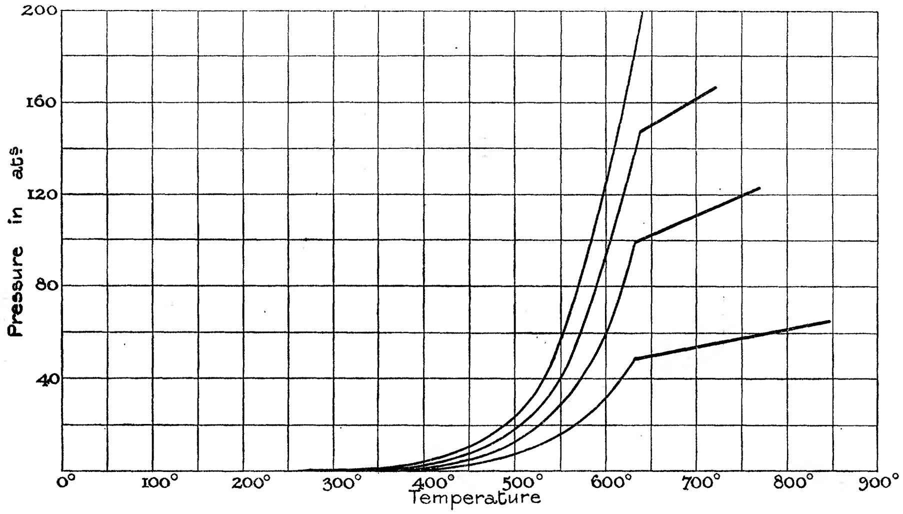

Fig. 6.—Isomers for Water Vapour.

If we follow one of these from low temperatures upwards, we see at once the enormous pressures necessary in order that a given surface may retain its layer of condensed material intact as the temperature rises.

A material such as charcoal, which condenses gases freely, will hold a certain weight of gas at any temperature and its corresponding pressure as given by its isoneres. If one follows an isonere from low to high temperatures, one can trace the character of the action of the charcoal in Sir James Dewar's beautiful method for obtaining high vacua by means of condensation in charcoal. It will be now seen how a weight of gas which would require an enormous pressure to cause it to condense on a given surface at high temperatures, can be held by the same surface at low temperatures at an exceedingly low pressure.

The Attraction of the Solid.—When the isoneres continue beyond the critical temperature, as is the case with air on glass, the attraction between the particles of the solid and those of the liquid must be supposed greater than that between the particles of the liquid itself. To take a simple case, imagine first a drop of the liquid in equilibrium with its vapour. The pressure cannot be lowered without evaporation taking place, but if we now suppose the central part of the drop replaced by, say, glass, leaving only a thin layer of liquid of a certain thickness, the pressure can be reduced, without evaporation occurring, to a definite value depending on the thickness of the layer of liquid left. Besides doing this we may pass along the isonere to temperatures beyond the critical at which the material unaided by the solid could not exist at all in the liquid state.

Some substances, for example resinous solids, may act the other way in this respect, requiring a greater pressure in order to retain a layer under the above circumstances.

Drying of Surfaces by Reduction in Pressure.—The relation as found by experiment between the vapour pressure and the weight condensed on a given surface, namely, the parabolic law, gives us for the rate of loss of moisture from a given surface with reduction in pressure

$$dw/dp = \kappa/(\mathrm{W}-w),$$

where W is the weight held at saturation. That is to say, the rate of loss with reduction in pressure is inversely proportional to the extent drying has proceeded. Looked at from this point of view, the experimental relation seems a suitable and likely one. For as drying proceeds the average distance from the solid to the remaining particles becomes less. The effect of the attraction of the solid in retaining the layer should thus be felt in increasing ratio.

If the law were known connecting the distance apart with the attraction between particles, that is to say, the Laplacian attraction, it might be possible to deduce the relations of the vapour pressure and the thickness of the condensed layer. Conversely, now that we know this relation experimentally, it suggests a possibility of determining the form of the function assumed by Laplace.

For example, let us make the supposition that inside the boundary of the liquid vapour surface the total pressure is always to be the same, that is to say, the sum of the intrinsic pressure and of the vapour pressure for every thickness of water layer is to be a constant quantity.

Thus $\mathrm{P} + \mathrm{K} = \mathrm{P}_0 + \mathrm{K}_0$, where P_0, is the saturation vapour pressure, and K_0 the intrinsic pressure due to an unlimited depth of water under the vapour, while P is the vapour pressure for a thickness of water layer (l), and K the intrinsic pressure partly due to this water layer and partly due to the solid beneath. We have, using the notation employed by Maxwell,*

$$K_0 = 2\pi\sigma^2\int_0^\infty \psi(z)\,dz, \quad \text{and} \quad K = 2\pi\sigma^2\int_0^l \psi(z)\,dz + 2\pi\sigma\sigma'\int_0^l \psi_1(z)\,dz,$$

where $\psi(z)$ and $\psi_1(z)$ are the functions proper for water-water and water-glass respectively, and σ, σ' the "densities" of water and glass.

The thickness of the layer of water in equilibrium with saturated vapour is probably in amount about that of the "molecular range," so that for lower pressures the solid must have an important effect. Parks,† however, gives the thickness of water layers on glass and other substances to be from 13 to 80 × 10^{-6} cm., which is greater than the commonly adopted value for the molecular range, though it is true that Quincke estimates the molecular range to be of about the same order, 50 × 10^{-6} cm. The method adopted by Parks makes it possible that some of the water supposed by him to be in the water layer was really held in capillary cavities of the character referred to earlier in this paper.

We may write

$$P_0 - P = 2\pi\sigma\left\{\sigma'\int_0^\infty \psi_1(z)\,dz - \sigma\int_0^\infty \psi(z)\,dz\right\}.$$

This gives us

$$\frac{dP}{dl} = 2\pi\sigma\,\{\sigma'\psi_1(l) - \sigma\psi(l)\}.$$

Assuming our experimental relation $(P_0 - P) = a\,(l_0 - l)^2$, where l_0 is the maximum thickness reached by the layer at saturation, and a is a constant, we have, if we take

$$\psi_1(l) = \psi(l), \qquad (\sigma' - \sigma)\,\psi(l) = b\,(l_0 - l).$$

This is the attraction per unit mass at a point situated at distance l from the plane surface of a substance of "density" $(\sigma' - \sigma)$ extending to infinity. Thus on the supposition made the law of force between two particles, as assumed by Laplace, must be such as to produce a resultant force $F = b\,(l_0 - l)$ at distance l from an infinite plane boundary of the substance, when l_0 is the molecular range or distance at which the force is insensible.

Explanation of Action of Hygroscopes.—The law of the coincidence of the isoneres and isohygrometrics throws light on the working of the various forms of hygroscopes, in which the alteration in length of hair or gut is employed. Thus these substances are wetted to the same extent for the same hygrometric state, so that, neglecting temperature effects and supposing the length to depend simply on the wetness, we can understand how these instruments afford approximately correct indications of the hygrometric state at all temperatures.

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* 'Ency. Brit.,' art. "Capillarity."

† 'Phil. Mag.,' vol. 5, p. 517.

The author has utilised directly the weight of moisture condensed on flannel for the purpose of constructing a recording hygrometer. The flannel is suspended on a recording balance. Its alterations in weight are thus registered. The amount held by the flannel alters with the temperature supposing the moisture in the atmosphere to remain constant, or supposing the temperature constant it alters with the amount of moisture, but, as we have seen, both may alter without changing the weight, provided the alteration is along an isohygrometric.

PART II.—*Measurement of the Vapour Pressure of Water at different Temperatures in Equilibrium with a Fabric wetted with a Constant Quantity of Water.*

The form of apparatus shown in fig. 7 was used by us in our experiments to investigate the relation between the temperature and the corresponding vapour pressure in equilibrium with a fabric wetted with a constant quantity of water. The material used was flannel, and the results obtained show that, at all temperatures within the limits of the experiments, the pressure of the vapour from it, when holding a constant weight of water, may be taken as being always the same fraction of the saturation pressure of water vapour.

The details of the apparatus are as follows:—A is a glass bulb of about 300 c.c. capacity for containing the material under examination. B is a side tube leading to the air pump with which the apparatus was evacuated. It was sealed off at the constriction when there was a good vacuum. C is a side tube to this provided with a tap, and ending in a bent-over sealed capillary. This served for the entrance of water.

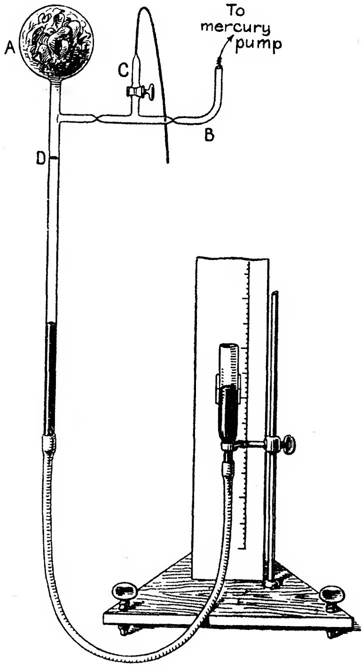

FIG. 7.

D is a fine hair tied round the stem (in a file mark) which served as a rough reference mark. The bulb is connected to a mercury manometer, the mercury level in which is read by means of a mirror at the back of the reservoir, with a fine line scratched across it. This line is made to coincide with the reflection of the mercury level and with the mercury level itself. The position on the scale is then read.

The heating arrangements (fig. 8) were as follows:—The bulb and the stem to below the mark were enclosed in a copper water bath, a rubber cork fitted into a short tube at the bottom allowed the rest of the barometer tube (of which the bulb was to form the top) to project below from the water bath. The mercury level during an experiment was always kept up to the mark; this part of the stem was always at the same temperature as the bulb, so that no condensation of steam took place on the mercury surface.

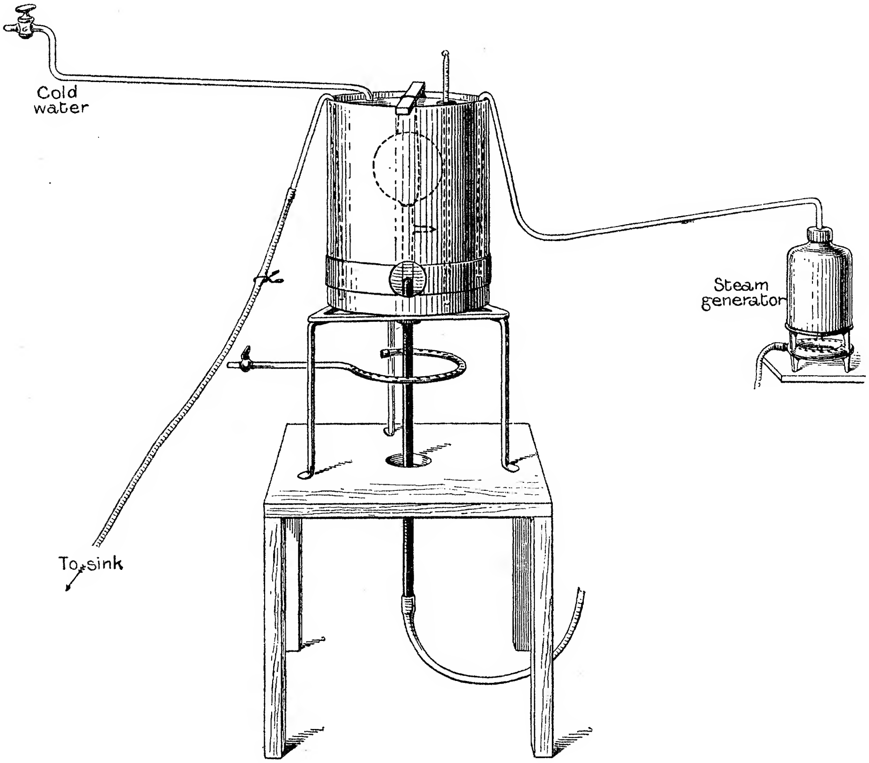

Fig. 8.

Two round windows of mica were made on opposite sides of the water bath; an electric glow lamp, surrounded by a piece of oiled paper, rendered the mercury surface visible through these windows. The horizontal cross wire of a cathetometer telescope was focussed on the barometer tube at the level of the hair; the hair served as the coarse, the cathetometer as the fine adjustment. By means of the cathetometer also this level was read on the scale of the pressure gauge, so that pressures could be read by reading the position of the surface of mercury in the reservoir, since during an experiment the upper level of mercury was kept constant.

Heating to any desired temperature was effected by means of steam, which helped also to stir the water. To aid in keeping the bath at any particular temperature, a ring-shaped gas burner placed beneath was also used. Cooling could be effected by drawing off hot water by a siphon and letting in cold from a tap. The bath was kept stirred, and readings of the pressure were taken when the temperature was steady at any particular point. The material used was about 10 grammes of freshly washed flannel. This was cut into strips and inserted into the bulb.

The method of introducing the water was as follows:—The capillary from tube C (fig. 7) was sealed off and the tap turned on. The apparatus was then evacuated by the pump, which was then sealed off. After turning off the tap of the tube C the end of the capillary was broken off under the surface of some freshly boiled distilled water in a beaker. Thus the tube, as far as the tap, was filled with water, and the required amount could be let into the apparatus without letting any air in. After it had evaporated into the bulb, the side tube was taken off at the constriction near the bulb. Then the apparatus was ready for experiment, but it will only serve to give one isonere or curve with the same weight of water present. Between each set of experiments it has to be reconstructed, freshly evacuated, and a fresh amount of water let in. The evacuation takes some time, as the air has a tendency to stick in the pores of the flannel. In several experiments a correction for residual air had to be applied.

In addition, a correction for capillarity was required owing to the size of tube employed. The chief source of error undoubtedly was uncertainty as to temperature of the flannel itself. Different values for the pressure were often got according as the temperature was reached from above or below.

The following table gives the results observed when the flannel contained nearly its maximum quantity of water. In column 1 are the temperatures, and in 2 the corresponding vapour pressures. The pressures of saturated vapour from Regnault's tables are given in column 3, and the ratio of the vapour pressures from the flannel to these is given in column 4. It will be seen that these ratios are approximately constant, and considering the difficulty of maintaining the temperature steady for long enough for equilibrium to obtain, the agreement with the suggested law of constant ratio may be looked upon as sufficiently proved.

Table I.

θ°.	p.	P.	p/P.	θ°.	p.	P.	p/P.
22·3	1·77	1·99	0·88	63·5	15·14	17·48	0·87
23·2	1·95	2·11	0·92	64·2	15·95	18·05	0·88
25·0	2·10	2·35	0·89	71·7	22·14	25·10	0·88
25·4	2·30	2·41	0·95	78·0	29·00	32·70	0·89
32·0	3·30	3·53	0·93	84·9	37·39	43·15	0·87
39·0	4·75	5·20	0·91	93·2	48·32	59·27	0·82
46·7	7·41	7·79	0·95	94·0	49·00	61·06	0·80
54·5	10·68	11·47	0·93				

These results are perhaps most conveniently examined when exhibited as in fig. 9. Here the top curve is that of the saturated vapour pressure. The second is the isohygrometric obtained by reducing the ordinates of the first in a constant ratio, namely, that of the mean of those in the last column in Table I. The points marked along the curve are those in column 2, and on the whole follow the curve.

In Table II are given the observations made when the flannel contains a less weight of water.

Table II.

	p.	P.	p/P.		p.	P.	p/P.
20·0	0·815	1·74	0·47	57·5	7·35	13·2	0·55
21·6	1·00	1·91	0·52	66·1	11·47	19·6	0·57
25·5	1·30	2·42	0·53	66·2	10·88	19·7	0·55
25·6	1·23	2·43	0·50	71·2	14·19	24·6	0·53
30·0	1·67	3·16	0·52	71·4	14·84	24·8	0·59
36·5	2·42	4·54	0·53	80·9	21·78	36·8	0·58
36·8	2·34	4·61	0·50	81·2	23·14	37·2	0·62
44·3	3·52	6·88	0·51	88·1	27·89	48·9	0·57
50·9	5·49	9·62	0·55	94·2	33·15	61·5	0·53
57·1	7·58	13·01	0·56	95·3	33·71	64·1	0·52

The third curve in fig. 9 is the isohygrometric drawn with the mean ratio obtained in Table II, the points as before being marked along it.

The observations in Table III were made with still less water present in the flannel.

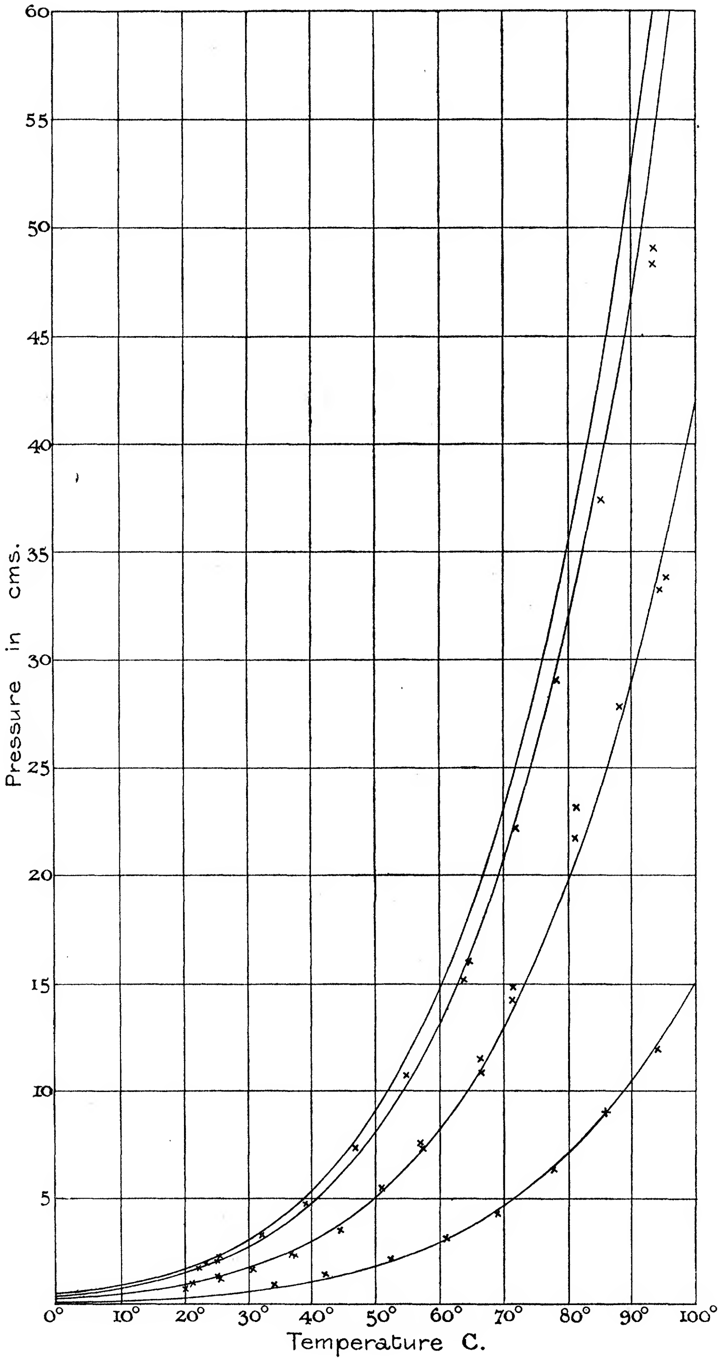
60
55
50
45
40
35
30
25
20
15
10
5
Pressure in cms.
0°
10°
20°
30°
40°
50°
60°
70°
80°
90°
100°
Temperature C.

Fig. 9.

Table III.

$\theta°$.	p.	P.	p/P.
33·9	0·97	3·93	0·24
41·8	1·46	6·04	0·24
52·2	2·15	10·25	0·20
61·0	3·16	15·59	0·20
69·0	4·31	22·34	0·19
77·6	6·36	31·17	0·20
87·8	8·96	48·30	0·18
93·7	11·94	60·39	0·19

The lowest curve is the isohygrometric plotted from the mean ratio of Table III. In this case the agreement of the points with the curve appears remarkably good, considering the experimental difficulties.

Observations and Photographs of Black and Grey Soap Films.

By Herbert Stansfield, B.Sc., Research Fellow of the University of Manchester.

(Communicated by Arthur Schuster, F.R.S. Received January 3,—Read January 25, 1906.)

[Plates 2—3.]

1. Some years ago, while working as a research student, in continuation of Reinold and Rücker's work on soap films, I made measurements on a large number of black films. The conditions of the experiments were not suitable for observing the thinner black, and I did not notice it, although I knew that it had been recorded by Newton, and that Reinold and Rücker* had not only seen the two blacks together, but had also obtained electrical observations indicating that the darker black was half the thickness of the other.

Three years later, Johonnott† published the results of optical measurements of black films, which showed that the thinner black was half the limiting thickness reached by the thicker black in the process of thinning.

On taking up the subject again rather more than a year ago, I wished to become familiar with the thinner black, and with this object examined flat

* 'Phil. Trans.,' A, vol. 184 (1893), p. 513.

† 'Phil. Mag.,' vol. 47 (1899), p. 501.